

REMARKS/ARGUMENTS

I. General Remarks

Applicants acknowledge with appreciation the care that the Examiner has given in responding to Applicants' response to her previous office action. The Examiner has discussed over eleven pages, exceeding even the length of the patent application itself, her reasons for denying allowance of any of Applicants' claims.

The Examiner has indicated in her response that Applicants have used terms that the Examiner views to be "not conventional terms of the art" [OA § 2 on page 2], or "not technically correct," [OA § 3 on page 2], and the Examiner has stated that it is "unclear" or "not clear" what Applicants mean [OA § 9 on page 6, and OA § 12 on page 9] and that Applicants' statements are "quite puzzling" [OA § 12 on page 8]. The Examiner has asked a number of times "what does it mean?" and has said she is "just perplexed." She has admonished "Applicants . . . [to] use conventional terminology of the field." [OA § 12 on page 10]

Considering the Examiner's high level of skill and expertise with NMR spectroscopy, and her focus on same, Applicants appreciate that the Examiner considers the above alleged faults to be those of Applicants and the undersigned counsel. However, Applicants respectfully traverse the Examiner's position, and Applicants respectfully submit that their application is simply in the **wrong art unit**. Instead of being in Art Unit 1797, Applicants respectfully submit that their application would be better understood in Art Unit 2862 or a similar art unit that reviews applications for nmr well logging methods and tools. Applicants respectfully request that the Examiner move the application to a more suitable art unit for further evaluation.

Notwithstanding this request, to provide a complete response to the office action, please consider the application in view of the following remarks.

II. Disposition of Claims

Claims 1, 8-14, 17, 18, 32, 37, 46 and 47 are pending. Applicants have amended claims 1, 8, 11, 13, 14, 32, and 37 herein.

III. Examiner's Response to Previous Amendment

The Examiner has objected under 35 U.S.C. § 132(a) to Applicants "amendment filed 12/17/08" because the Examiner views the "amendment" to introduce "new matter into the disclosure." The Examiner states that, "The added material which is not supported by the original disclosure is as follows: 'identifying the shift in the NMR response that distinguishes the drilling fluid from formation fluid.'" The Examiner then goes on to state that, "While the terms used by the Applicants are not conventional terms of the art, the examiner interprets this as changing chemical shift of the NMR signal upon adding of the paramagnetic species, which is not disclosed in the specification." The Examiner states that, "The specification discloses only changes in T2 relaxation time, rather than changes in NMR chemical shifts." The Examiner has required cancelation of this alleged "new matter."

Applicants respectfully traverse this objection by the Examiner. By the Examiner's reference to the "amendment," Applicants understand that the Examiner has objected to a step added to the claims for "identifying the shift in the NMR response that distinguishes the drilling fluid from formation fluid hydrocarbons." This step is supported in the original specification of the application. In paragraph [0009], Applicants teach:

[0009] The present invention provides a nuclear magnetic resonance (NMR) method for detecting the presence and preferably also the amount of any invasion or filtration of oil-based drilling fluid into a subterranean formation from a borehole penetrating the formation and drilled with the drilling fluid. That is, the present invention provides a method for distinguishing native or residual hydrocarbons in a formation from oil-based drilling fluid so that the drilling fluid does not distort the detection or measurement of such hydrocarbons using nuclear magnetic resonance.

In paragraph [0011], Applicants teach:

[0011] The paramagnetic species shorten the NMR/T1 and T2 responses of the oil or synthetic base comprising the drilling fluid to 10-100 milliseconds at typical formation or laboratory temperatures thereby causing the response to be sufficiently different from the NMR/T1 and T2 responses of native or residual hydrocarbons to distinguish them. Generally, the change in T1 and T2 relaxation rates for the drilling fluid is proportional to the concentration of paramagnetic species present.

And in paragraph [0023], Applicants teach, in part:

... addition of even a small amount of oil soluble or oil solubilized paramagnetic species to oil-based drilling fluid causes a shift in the NMR response that distinguishes the drilling fluid from formation hydrocarbons. Preferably an amount of the paramagnetic species is used so that a quantitative determination of any drilling fluid that filters into the formation may be made as well as detection of the drilling fluid in the formation.

(emphasis added).

The Examiner is requested to withdraw her objection under 35 U.S.C. 132(a).

IV. Objection to Specification

The Examiner has objected to statements in Applicants' specification. Specifically, the Examiner has stated that the specification discloses "statements that are not technically correct."

The Examiner then explains as follows:

For example, the statement that "persistent organic radicals are free electrons" is not a correct statement (see page 5, paragraph [0020].) The radicals are not "free electrons." Free electrons (especially flowing free electrons) are an electrical current. Free electrons have nothing to do with radicals. Radicals are rather atoms with an unpaired electron. There is a conventional term "stable radicals"—is that, what is meant by the name "persistent radicals?" The radical cannot "pair" with another electron. The radical can "pair" with another radical. Therefore, the statement is misleading and incorrect."

Applicants respectfully object to this objection by the Examiner, made by the Examiner for the first time in this third office action in this case, contrary to Patent Office policy. MPEP 707.07(g) specifies that, "Piecemeal examination should be avoided as much as possible." Moreover, Applicants respectfully traverse the Examiner's position concerning Applicants' teachings in paragraph 10, a position which the Examiner has apparently stated as "common

knowledge” or as “official notice” pursuant to MPEP § 2144.03 without documentary evidence.

In paragraph [0010], Applicants state:

[0010] In the method, oil solubilized “paramagnetic species” are added to the drilling fluid during drilling of the borehole. As used herein, the term “paramagnetic species” shall be understood to mean any chemical entity, molecule or ion comprising any transition metal, and/or lanthanum and/or other rare earth metal, that has paramagnetic character, and/or any persistent organic radical that has paramagnetic character. Persistent organic radicals are free electrons that “persist” or linger as free or do not quickly or immediately pair with other electrons. The paramagnetic species used in the invention are preferably selected from the group consisting of Fe^{3+} , Mn^{2+} , Ni^{2+} , and Cu^{2+} , Gd^{3+} , and 2,2,6,6-tetramethylpiperidineyl-1-oxyl (also called “TEMPO”) ions, and mixtures thereof, and are preferably selected with characteristics of the formation in mind so that the paramagnetic species selected will be of the type that will not interact with the formation. Preferably a sufficient amount of the paramagnetic species is used so that a quantitative determination of any drilling fluid that filters into the formation may be made as well as detection of the drilling fluid in the formation.

Wikipedia explains “radical” in chemistry as follows:

In chemistry, **radicals (often referred to as free radicals) are atoms, molecules, or ions with unpaired electrons** on an otherwise open shell configuration. These unpaired electrons are usually highly reactive, so radicals are likely to take part in chemical reactions. Radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes, including human physiology. . . .

Historically, the term *radical* has also been used for bound parts of the molecule, especially when they remain unchanged in reactions. These are now called functional groups. For example, methyl alcohol was described as consisting of a methyl “radical” and a hydroxyl “radical.” Neither are radicals in the modern chemical sense, as they are permanently bound to each other, and have no unpaired, reactive electrons. . . .

[http://en.wikipedia.org/wiki/Radical_\(chemistry\)](http://en.wikipedia.org/wiki/Radical_(chemistry)) (bold emphasis added; italics in original) (Exhibit A); also see http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B7g... (Exhibit B).

Applicants respectfully submit that their paragraph [0010] is not inconsistent with the “common knowledge” expressed in Wikipedia, and by the examples and context provided in paragraph [0010], one of ordinary skill in the applicable art would understand the paragraph and not find it to be “misleading.” To address the Examiner’s concern, which Applicants understand

to be intended for clarification, Applicants propose the following minor amendment, changing the word “are” to “have”:

[0010] In the method, oil solubilized “paramagnetic species” are added to the drilling fluid during drilling of the borehole. As used herein, the term “paramagnetic species” shall be understood to mean any chemical entity, molecule or ion comprising any transition metal, and/or lanthanum and/or other rare earth metal, that has paramagnetic character, and/or any persistent organic radical that has paramagnetic character. Persistent organic radicals ~~are~~ have free electrons that “persist” or linger as free or do not quickly or immediately pair with other electrons. The paramagnetic species used in the invention are preferably selected from the group consisting of Fe^{3+} , Mn^{2+} , Ni^{2+} , and Cu^{2+} , Gd^{3+} , and 2,2,6,6-tetramethylpiperidineyl-1-oxyl (also called “TEMPO”) ions, and mixtures thereof, and are preferably selected with characteristics of the formation in mind so that the paramagnetic species selected will be of the type that will not interact with the formation. Preferably a sufficient amount of the paramagnetic species is used so that a quantitative determination of any drilling fluid that filters into the formation may be made as well as detection of the drilling fluid in the formation.

Since the meaning of this change is already believed to be understood from the context of the paragraph and general knowledge in the art, this correction is not believed to add new matter to the specification and the Examiner is respectfully requested to enter it and to withdraw her objection.

V. Claim Objections

The Examiner has again objected to claim 10 as being of improper dependent form for failing to further limit the subject matter of a previous claim. The Examiner has stated again that, “Claim 10 recites taking at least one core sample from the region of said formation, which is inherent to the parent claim, since the parent claim recites analyzing the formation, which inherently requires taking the sample for analysis.”

In response to the previous office action, Applicants traversed the Examiner’s rejection, reasoning as follows:

Applicants teach in their specification, for example paragraphs 25 and 27, that analysis of the formation can be conducted by taking core samples from the formation for

analysis, by conducting testing or logging of the formation with an NMR wireline tool in the borehole, or both. Thus, Applicants respectfully submit that formation analysis does not require core sampling and thus the step of analyzing the formation does not inherently require the taking of core samples for analysis.

The Examiner responded to Applicants' position at page 7 of her office action. The Examiner stated:

Analysis of a sample requires "taking the sample" for analysis, specifically 'a core sample from the region of said formation' for analysis of the formation fluid. It does not matter, *how* this sample is taken; the fact is that it has to be taken to be analyzed. Claim 10 only recites 'taking at least one core sample from the region of said formation'-the step, without which performing the method of the parent claim is impossible.

Applicants again respectfully traverse this objection by the Examiner as stated above. Applicants respectfully submit that the Examiner has made an alleged factual assertion without proper official notice and without proper basis upon common knowledge as described in MPEP § 2144.03. Moreover, Applicants respectfully submit that the Examiner's assertion is incorrect. The present patent application was written for one of ordinary skill in the *relevant* art to understand. One of such skill would understand that claim 1 does **not** call for a taking of a core sample or for analysis of a core sample. Applicants respectfully submit some general background information about NMR tools and well logging copied from the internet for the Examiner's consideration and better understanding of the *relevant* art. http://en.wikipedia.org/wiki/Well_logging (Exhibit C); <http://www.aapg.org/explorer/2000/12dec/tools.cfm> (Exhibit D).

V. Claim Rejections—35 U.S.C. § 112

The Examiner has rejected claims 1, 8-14, 17-18, 32, and 37, and 46-47 under 35 U.S.C. § 112, first paragraph, as failing to comply with the written description requirement. The Examiner then characterizes Applicants' specification in her words and own understanding, rather than using the Applicants' own teachings. Again, Applicants respectfully traverse the

Examiner's reliance on common knowledge or taking of official notice of matters without documentary evidence. MPEP § 2144.03. Applicants respectfully submit that the Examiner mischaracterizes Applicants' claims and their supporting specification because the Examiner relies on her own knowledge and experience which is not based in the relevant art—the art of drilling and **testing of subterranean boreholes** or oil wells for the detection and recovery of hydrocarbons from subterranean formations.

More specifically, the Examiner states that Applicants' specification “does not show any ‘shift in the NMR response’ as provided in claim 1. Applicants disagree.

Paragraph [0022] of Applicants specification states:

[0022] The method of the invention requires doping of the oil-based drilling fluid with oil soluble or oil solubilized paramagnetic species. Generally, the greater the concentration of such paramagnetic species in the fluid, the greater the enhancement in the contrast in NMR response of the drilling fluid when compared to the NMR response of formation hydrocarbons. However, addition of **even a small amount of oil soluble or oil solubilized paramagnetic species to oil-based drilling fluid causes a shift in the NMR response that distinguishes the drilling fluid from formation hydrocarbons.** Preferably an amount of the paramagnetic species is used so that a quantitative determination of any drilling fluid that filters into the formation may be made as well as detection of the drilling fluid in the formation.

(emphasis added).

Paragraphs [0030] – [0032] of Applicants' specification state:

[0030] Samples of ACCOLADE® synthetic oil base containing (or doped with) different concentrations of CONOSTAN® Mn organo-metallic standard and samples of ACCOLADE® synthetic oil base containing different concentrations of CONOSTAN® Fe organo-metallic standard were prepared. These samples were tested with NMR equipment and the results are graphed in Figure 1. **The NMR relaxation times were significantly affected by the presence of the paramagnetic ion doping agent, even in relatively small concentrations.** For example, just 50 ppm of the Mn⁺⁺ reduced the T2 for the ACCOLADE® fluid about 50%.

[0031] **Figures 2, 3, and 4 compare the NMR data and T2 inversion for the ACCOLADE® drilling fluid without any dopant (Fig. 2(a) and Fig. 2(b)), and for the ACCOLADE® drilling fluid with 384 ppm iron ions (from CONOSTAN® Fe organo-metallic standard) added therein (Fig. 3(a) & Fig. 3(b)), and for the ACCOLADE®**

drilling fluid with 384 ppm manganese ions (from CONOSTAN® Mn organo-metallic standard) added therein (Fig.4(a) and Fig. 4(b)). The effect of the dopant on the response of the drilling fluid is significant, demonstrating by this comparison the utility of adding the paramagnetic species to the drilling fluid as a tracer for detecting the drilling fluid in the formation.

[0032] The principles of the invention may be applied to techniques for taking NMR measurements with wireline tools run downhole in a borehole drilled with oil-based fluid, including without limitation logging while drilling tools. The principles of the invention may also be applied to laboratory techniques for NMR analysis of core samples taken from a subterranean formation. The principles of the invention may also be applied to techniques for taking NMR measurements downhole at locations of a formation where core samples are taken for further analysis or testing in the laboratory.

(emphasis added).

Figures 1, and Figures 2(a) & (b), 3(a) & (b) and 4(a) & (b) in the specification, as described in the specification in the above paragraphs and in the following paragraphs [0014]-[0020], show the shift recited in the claims upon review—that is, see Figure 1 and also compare Figures 2(a) & (b) with Figures 3(a) & (b) and compare Figures 2(a) & (b) with Figures 4(a) & (b).

[0014] Figure 1 is a graph of the measure of the T2 (NMR) response as a function of the concentration of paramagnetic iron and manganese ions in an oil-based drilling fluid.

[0015] Figure 2(a) is a graph of NMR data for an oil based drilling fluid.

[0016] Figure 2(b) is a graph of the T2 inversion response of an oil-based drilling fluid.

[0017] Figure 3(a) is a graph of NMR data for an oil-based drilling fluid doped with 384 ppm Fe^{3+} ions solubilized in an organic fluid.

[0018] Figure 3(b) is a graph of a T2 inversion response for an oil-based drilling fluid doped with 384 ppm Fe^{3+} ions solubilized in an organic fluid.

[0019] Figure 4(a) is a graph of NMR data for an oil-based drilling fluid doped with 384 ppm Mn^{2+} ions solubilized in an organic fluid.

[0020] Figure 4(b) is a graph of a T2 inversion response for an oil-based drilling fluid doped with 384 ppm Mn^{2+} ions solubilized in an organic fluid.

Applicants respectfully submit that they do teach a “shift in the NMR response” as claimed. It is the Examiner, not Applicants, who states that “there is signal broadening, which is not changing the chemical shift.” Applicants do not discuss signal broadening or chemical shifts. Applicants respectfully traverse the Examiner’s inclusion of matters she apparently views to be “common knowledge” or ripe for “official notice” without documentary evidence. See MPEP § 2144.03. Applicants respectfully traverse the Examiner’s rejection of Applicants’ claims based on such unsupported conclusions by the Examiner, apparently derived from and/or based on her personal knowledge, which are inconsistent with Applicants’ data provided in Applicants’ specification, data that fully supports Applicants’ claims.

The Examiner also argues that Applicants’ “specification does not disclose, as to how it is possible to distinguish oil based drilling fluid comprising paramagnetic species from subterranean formation fluid hydrocarbons, when the oil based drilling fluid readily intermixes with the formation hydrocarbons, when the latter being susceptible to exactly the same influence of paramagnetic species, as the drilling fluid, and with the same effect of paramagnetic species on the NMR spectra lines, as for the oil drilling fluid.” The Examiner states that Ramakrishnan (US Patent No. 7,134,500) notes that when a well is drilled with oil-based mud the filtrate may miscibly mix with the formation fluid. The Examiner then again takes “official notice” objectionably without evidentiary support that “It is well known for a person of ordinary skill in the art (as well as for a person skilled in the art and for an expert in the art) that the presence of even traces of paramagnetic impurities in the sample leads to a significant broadening of NMR spectral lines.”

Applicants respectfully traverse the Examiner's position. Ramakrishnan is concerned with a laboratory technique, not with field testing. Moreover, the passage cited by the Examiner, at column 1, lines 48-50, is specifically directed to the problem of oil based mud filtrate mixing with formation fluid samples. Applicants seek to address the problem with steps taken in the field rather than after the fact in the laboratory.

Applicants teach, for example, in paragraph [0026]:

Preferably, the particular paramagnetic species selected will be selected with the other components of the fluid in mind so that the paramagnetic species will not interact with any such components in such a way as to unfavorably alter the rheological characteristics of the fluid or any other characteristics of the fluid considered desirable for the intended use of the fluid. Further, the particular paramagnetic species selected will preferably be selected with the other components of the fluid in mind so that the paramagnetic species will not interact with any such components in such a way as to alter or interfere with the paramagnetic character of the paramagnetic species or the solubility or solubilization of the paramagnetic species in oil. Also, as previously noted, preferably the paramagnetic species chosen will be the type that will not interact with the formation in which the drilling fluid will be used.

The Examiner also objects to the preambles of Applicants claims 8-10, 11-13, 14-18, and 32-37. Such preambles are commonly used in the *relevant* art and are well by persons of ordinary skill in the applicable art. The law is well established that the specification does not have to include material that persons of ordinary skill in the applicable art would understand without its inclusion. Moreover, Applicants respectfully submit that the preamble of claim 8 (and thus dependent claims 9 and 10), referring to "detecting hydrocarbon-bearing zones" has support in paragraph [0021] cited by the Examiner, specifically referring to "a method . . . so that hydrocarbons may be detected" Similarly, the preamble of claim 11 (and thus dependent claims 12 and 13) has support in paragraph [0021] in referring to "a method . . . of detecting . . . hydrocarbons in the formation" With respect to the preamble of claim 14 (and thus dependent claims 17 and 18, claims 15 and 16 having been previously canceled), and claim 32

(and thus dependent claim 37, claims 33-36 having been previously canceled), see for example of support paragraph [0025] of Applicants' specification which states in part:

For another example, if an NMR wireline tool is to be used for downhole testing in the borehole, then the paramagnetic species might be added to the drilling fluid before or at about the same time the drilling of the borehole is begun or at some later time during drilling of the borehole. Again, however, the paramagnetic species should be added to the drilling fluid before drilling through the portion of the formation to be tested.

Also see paragraph [0027] of Applicants' specification which states:

[0027] A preferred method of drilling a borehole in a subterranean formation either containing hydrocarbons or in search for hydrocarbons, and in which use of an oil-based drilling fluid is desired, will use an oil-based drilling fluid comprising paramagnetic species soluble or solubilized in the oil base. Such method allows for logging of the formation and/or core sampling of the formation for analysis of the presence and/or quantity of hydrocarbons using nuclear magnetic resonance techniques at any time and at any point along the borehole.

After rejecting claims 1, 8-14, 17-18, 32, and 37, and 46-47 under 35 U.S.C. § 112, first paragraph, the Examiner rejected all of the same claims under 35 U.S.C. § 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter regarded as the invention.

Again, the Examiner stated that claims 1, 8, 11, 14, 32 and 37 recite "shift in the NMR response" and she does not know what that phrase means. Applicants respectfully submit that the specification explains this "shift" in words and figures and Applicants refer the Examiner to the discussion above made in response to the Examiner's rejection under 35 U.S.C. § 112, first paragraph. For example, see Applicants' specification at paragraphs [0022], [0030]-[0032], Figures 1, 2(a) and (b), 3(a) and (b), and 4(a) and (b), and paragraphs [0014] – [0020].

The Examiner also complains that Claim 14 "recites 'a process of analyzing the fluid composition of a subterranean formation'" and that "Conventionally subterranean formations are complex mixtures of hydrocarbons with overlapping signals in NMR spectra." The Examiner

states that Applicants' specification does not provide any disclosure for this type of analysis or the metes and bounds of the claim.

Applicants respectfully traverse this rejection of claim 14 and respectfully submit that the law is well established that claims must be read in light of the entire specification. When this is done, the claim is clear and definite. Applicants are not concerned with a detailed laboratory NMR analysis of the components of crude oil as perhaps in the Examiner's experience in other cases. Applicants are simply concerned with detecting drilling fluid filtrate in the formation as stated in the claim and in the specification and in distinguishing the drilling fluid from the formation fluid hydrocarbons as stated in the claim and in the specification. The above discussion traversing the Examiner's rejections under 35 U.S.C. § 112, first paragraph, are also applicable to these rejections by the Examiner under 35 U.S.C. § 112, second paragraph.

With respect to the Examiner's comments regarding the appropriate art unit for this application, Applicants recommend an art unit that reviews applications for nmr well logging methods and tools.

With respect to the Examiner's puzzle of the undersigned's statement in her response to the previous office action referring to "NMRs", the undersigned advises that she used NMRs in the statements the Examiner questioned as a noun and that NMRs referred to NMR devices. One of ordinary skill in the *relevant* art for this patent application well understands the difference in NMR devices used in the oil field as in Applicants' invention and NMR devices or equipment used in the sophisticated analytical laboratories of the Examiner's reported experience. Reference to the "NMRs" used in the field having only about 1 Hz was to explain that NMR devices used in the oilfield are "low power" compared to the NMR equipment with which the Examiner is familiar.

The undersigned has not indicated that the Examiner could not understand logging and drilling. However, sophisticated NMR laboratory experience is not helpful in relating the use of NMR to the oilfield, and particularly to the use of NMR logging equipment. A subterranean formation is very different from a test tube in a laboratory.

VI. Claim Rejections—35 U.S.C. § 102/103

The Examiner has rejected claims 1, 8-14, 17-18, 32, 37, and 46-47 under 35 U.S.C. § 102(b) as anticipated by, or under 35 U.S.C. § 103 as obvious from, Kleinberg (U.S. 6,346,813). Applicants respectfully traverse these rejections for the reasons stated in response to the previous office actions.

Applicants respectfully submit that Kleinberg does not teach the paramagnetic species that Applicants teach and that Kleinberg does not enable Applicants' invention. Kleinberg teaches that:

Dissolved paramagnetic compounds will reduce the proton relaxation times of oils. Thus if two oils have the same viscosity, they will have different relaxation times if they have substantially different paramagnetic content. While many crude oils and most oil base mud filtrates have negligible magnetic content, some crude oils have significant amounts of vanadium or nickel [Tissot and Welte, "Petroleum Formation and Occurrence", Springer-Verlag, 1978, Figure IV.1.20]. Because the relaxation effect is proportional to paramagnetic concentration, the proportions of two oils in a mixture can be monitored. Deliberate introduction of an oil-soluble paramagnetic substance into the oil base mud can considerably enhance this effect when the native crude is relatively free of paramagnetic material.

Kleinberg, Col. 8, lines 5-18.

Applicants teach the specific paramagnetic species that will enable identification of a shift in the NMR response that distinguishes the drilling fluid from formation hydrocarbons. Preferably an amount of the paramagnetic species is used so that a quantitative determination of any drilling fluid that filters into the formation may be made as well as detection of the drilling fluid of the formation. However, even addition of a small amount of oil soluble or oil solubilized

paramagnetic species to oil-based drilling fluid causes the detectable and identifiable shift.

Paragraph [0022] of Applicants' specification.

Applicants' invention affords or enables detection of or distinguishing of drilling fluid from formation fluids when the drilling fluid and the formation fluids have different viscosities, as well as the same viscosity.

While there is mixing between the formation fluids and the drilling fluid, there is not an equilibrium in the subterranean formation during drilling and the drilling fluid is not infinitely diluted in the formation fluid. Rather, there are regions of drilling fluid and regions of formation fluids—of pure native or residual hydrocarbons, i.e., formation oil. Under these circumstances, the shifting of the NMR response—the moving of where the peak comes out—is far more important in distinguishing the drilling fluid from the formation fluids than is the more or less broadening of the lines or peaks as seen with Kleinberg.

Applicants continue to traverse the Examiner's requirement for a "comparative analysis of the claimed subject matter of the instant invention vs. the disclosure" of Kleinberg, "with specific indication of distinctions between these disclosures." Further, Applicants respectfully submit that the Examiner's statement that it is "Applicants **duty** to perform corresponding comparative analysis of the claim language and the disclosure of the prior art in order to specifically indicate differences between the claim language and the disclosure" lacks support in MPEP § 714.02 cited by the Examiner, and Applicants respectfully traverse this position by the Examiner which is not a statement of applicable law. (emphasis by Examiner). Applicants respectfully submit that they have fully complied with this section of the MPEP and the law in distinguishing Kleinberg. Applicants respectfully submit that it is **error** for the Examiner to order unduly burdensome and costly testing and comparative data from Applicants. Again,

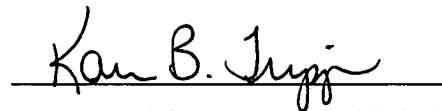
Applicants remind the Examiner that oilfield testing is very different from running an NMR analysis in a laboratory. Moreover, Applicants would have to use the benefit of their own invention to make this comparative analysis, which would be improper use of hindsight.

SUMMARY

Applicants respectfully submit that the claims as amended are now in condition for allowance and Applicants respectfully request the Examiner to allow the application to proceed to issue.

Respectfully submitted,

Date: July 28, 2009

A handwritten signature in black ink, reading "Karen B. Tripp", is written over a horizontal line.

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EXHIBIT A

Radical (chemistry)

From Wikipedia, the free encyclopedia

In chemistry, **radicals** (often referred to as **free radicals**) are atoms, molecules, or ions with unpaired electrons on an otherwise open shell configuration. These unpaired electrons are usually highly reactive, so radicals are likely to take part in chemical reactions. Radicals play an important role in combustion, atmospheric chemistry, polymerization, plasma chemistry, biochemistry, and many other chemical processes, including human physiology. For example, superoxide and nitric oxide regulate many biological processes, such as controlling vascular tone. "Radical" and "free radical" are frequently used interchangeably, although a radical may be trapped within a *solvent cage* or be otherwise bound. The first organic free radical identified was triphenylmethyl radical, by Moses Gomberg in 1900 at the University of Michigan.

Historically, the term *radical* has also been used for bound parts of the molecule, especially when they remain unchanged in reactions. These are now called functional groups. For example, methyl alcohol was described as consisting of a methyl "radical" and a hydroxyl "radical". Neither are radicals in the modern chemical sense, as they are permanently bound to each other, and have no unpaired, reactive electrons. They can, however, be observed as radicals in mass spectrometry after breaking down the substance with a hail of energetic electrons.

Contents

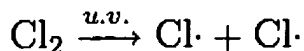
- 1 Depicting radicals in chemical reactions
- 2 Formation
- 3 Persistence and stability
- 4 Reactivity
- 5 Combustion
- 6 Polymerization
- 7 Atmospheric radicals
- 8 Free radicals in biology
 - 8.1 Reactive oxygen species
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Moses Gomberg, the founder
of radical chemistry
(1866-1947)

Depicting radicals in chemical reactions

In written chemical equations, free radicals are frequently denoted by a dot placed immediately to the right of the atomic symbol or molecular formula as follows:



Chlorine gas can be broken down by ultraviolet light to form atomic chlorine radicals.

Radical reaction mechanisms use single-headed arrows to depict the movement of single electrons:



The homolytic cleavage of the breaking bond is drawn with a 'fish-hook' arrow to distinguish from the usual movement of two electrons depicted by a standard curly arrow. It should be noted that the second electron of the breaking bond also moves to pair up with the attacking radical electron; this is not explicitly indicated in this case.

In chemistry, free radicals take part in radical addition and radical substitution as reactive intermediates. Chain reactions involving free radicals can usually be divided into three distinct processes: *initiation*, *propagation*, and *termination*.

- **Initiation** reactions are those which result in a net increase in the number of free radicals. They may involve the formation of free radicals from stable species as in Reaction 1 above or they may involve reactions of free radicals with stable species to form more free radicals.
- **Propagation** reactions are those reactions involving free radicals in which the total number of free radicals remains the same.
- **Termination** reactions are those reactions resulting in a net decrease in the number of free radicals. Typically two free radicals combine to form a more stable species, for example: $2\text{Cl}\cdot \rightarrow \text{Cl}_2$

Formation

The formation of radicals may involve breaking of covalent bonds homolytically, a process that requires significant amounts of energy. For example, splitting H_2 into $2\text{H}\cdot$ has a ΔH° of +435 kJ/mol, and Cl_2 into $2\text{Cl}\cdot$ has a ΔH° of +243 kJ/mol. This is known as the homolytic bond dissociation energy, and is usually abbreviated as the symbol DH° . The bond energy between two covalently bonded atoms is affected by the structure of the molecule as a whole, not just the identity of the two atoms, and radicals requiring more energy to form are less stable than those requiring less energy. Homolytic bond cleavage most often happens between two atoms of similar electronegativity. In organic chemistry this is often the O-O bond in peroxide species or O-N bonds.

However, propagation is a very exothermic reaction. Note that most species are electrically neutral although radical ions do exist.

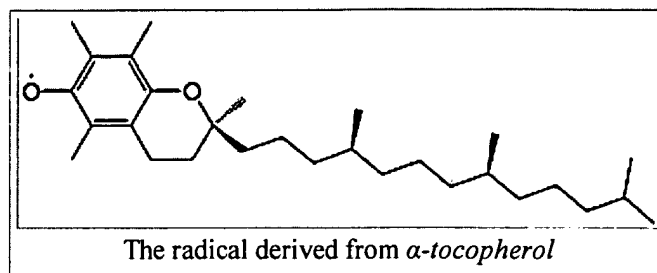
Radicals may also be formed by single electron oxidation or reduction of an atom or molecule. An example is the production of superoxide by the electron transport chain. Early studies of organometallic chemistry, especially tetra-alkyl lead species by F.A. Paneth and K. Hahnfeld in the 1930's supported heterolytic fission of bonds and a radical based mechanism.

Persistence and stability

Long lived radicals can be placed into two categories

■ Stable Radicals

The prime example of a stable radical is molecular dioxygen O_2 . Organic radicals can be long lived if they occur in a conjugated π system, such as the radical derived from α -tocopherol (vitamin E). There also exist hundreds of known examples of thiazyl radicals which show remarkable kinetic and thermodynamic stability, with only a very limited extent of π resonance stabilization ^{[1][2]}.



■ Persistent Radicals^[3]

Persistent radical compounds are those whose longevity is due to steric crowding around the radical center and makes it physically difficult for the radical to react with another molecule. Examples of these include Gomberg's triphenylmethyl radical, Fremy's salt (Potassium nitrosodisulfonate, $(KSO_3)_2NO\cdot$), nitroxides, (general formula $R_2NO\cdot$) such as TEMPO, verdazyls, nitronyl nitroxides, and azephenylenyls and radicals derived from PTM (perchlorophenylmethyl radical) and TTM (tris(2,4,6-trichlorophenylmethyl radical). The longest-lived free radical is melanin, which may persist for millions of years. Persistent radical are generated in great quantity during combustion, and "may be responsible for the oxidative stress resulting in cardiopulmonary disease and probably cancer that has been attributed to exposure to airborne fine particles." PMID 18678037^[4]

- Diradicals are molecules containing two radical centers. Multiple radical centers can exist in a molecule. In fact, much to the surprise of many, molecular oxygen naturally (i.e. atmospheric dioxygen) exists as a diradical (in its ground state as triplet oxygen). The high reactivity of atmospheric oxygen is owed somewhat to its diradical state (albeit non-radical states of dioxygen are actually less stable). The existence of atmospheric molecular oxygen as a triplet-state genuine radical results in its paramagnetic character, which can be easily demonstrated, i.e. by attraction of oxygen to an external magnet. (Note however that paramagnetism does not necessarily imply radical character.)

Reactivity

Radical alkyl intermediates are stabilized by similar criteria as carbocations: the more substituted the radical center is, the more stable it is. This will direct their reactions: formation of a tertiary radical ($R_3C\cdot$) is favored over secondary ($R_2HC\cdot$) or primary ($RH_2C\cdot$). However, radicals next to functional groups, such as carbonyl, nitrile, and ether are even more stable than tertiary alkyl radicals.

Radicals attack double bonds, but unlike similar ions, they are not as much directed by electrostatic interactions. For example, the reactivity of nucleophilic ions with α,β -unsaturated compounds ($C=C-C=O$) is directed by the electron-withdrawing effect of the oxygen, resulting in a partial positive charge on the carbonyl carbon. There are two reactions that are observed in the ionic case: the carbonyl is attacked in a direct addition to carbonyl, or the vinyl is attacked in conjugate addition, and in either case, the charge on the nucleophile is taken by the oxygen. Radicals add rapidly to the double bond, and the resulting α -radical carbonyl is relatively stable; it can couple with another molecule or be oxidized. Nonetheless, the

electrophilic/neutrophilic character of radicals has been shown in a variety of instances (e.g., in the alternating tendency of the copolymerization of maleic anhydride (electrophilic) and styrene (slightly nucleophilic).

In intramolecular reactions, precise control can be achieved despite the extreme reactivity of radicals. Radicals will attack the closest reactive site the most readily. Therefore, when there is a choice, a preference for five-membered rings is observed: four-membered rings are too strained, and collisions with carbons five or more atoms away in the chain are infrequent.

Combustion

Probably the most familiar free-radical reaction for most people is combustion. The oxygen molecule is a stable diradical, best represented by $\cdot\text{O}-\text{O}\cdot$, which is stable because the spins of the electrons are parallel. The ground state of oxygen is an unreactive spin-unpaired (triplet) diradical, but an extremely reactive spin-paired (singlet) state is available. In order for combustion to occur, the energy barrier between these must be overcome. This barrier can be overcome by heat, requiring high temperatures.

Combustion is comprised of various radical chain reactions that the singlet radical can initiate. The flammability of a given material is strongly dependent on the concentration of free radicals that must be obtained before initiation and propagation reactions dominate leading to combustion of the material. Once the combustible material has been consumed, termination reactions again dominate and the flame dies out. Propagation or termination reactions can be promoted to alter flammability. Tetraethyl lead was once commonly added to gasoline, because lead itself deactivates free radicals in the gasoline-air mixture. This prevents the combustion from initiating in an uncontrolled manner or in unburnt residues (engine knocking) or premature ignition (preignition).

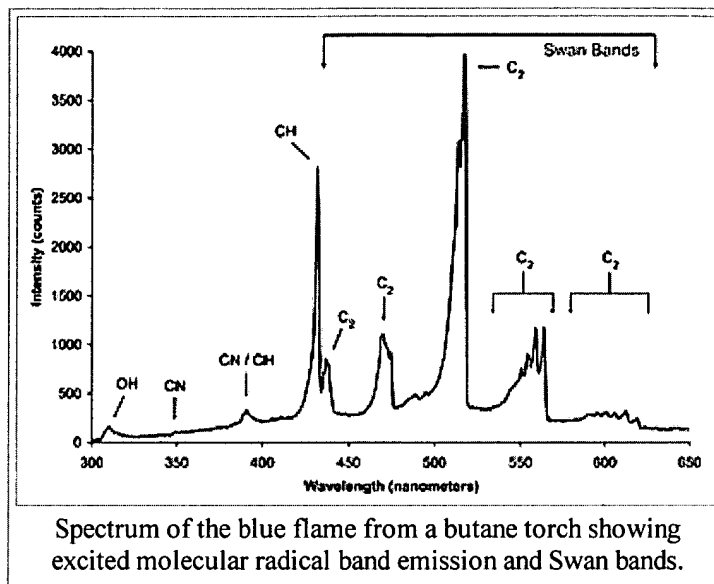
When a hydrocarbon is burned, a large number of different oxygen radicals are involved. The first thing to form is a hydroperoxide radical ($\text{HOO}\cdot$), which reacts further into hydroperoxides that break up into hydroxide radicals.

Polymerization

In addition to combustion, many polymerization reactions involve free radicals. As a result many plastics, enamels, and other polymers are formed through radical polymerization.

Recent advances in radical polymerization methods, known as Living Radical Polymerization, include:

- Reversible Addition-Fragmentation chain Transfer (RAFT)
- Atom Transfer Radical Polymerization (ATRP)



- Nitroxide Mediated Polymerization (NMP)

These methods produce polymers with a much narrower distribution of molecular weights.

Atmospheric radicals

The most common radical in the lower atmosphere is molecular dioxygen. Other free radicals are produced through photodissociation of source molecules. In the lower atmosphere the most important examples are the photodissociation of nitrogen dioxide to give an oxygen atom and nitric oxide which plays a key role in smog formation and the photodissociation of ozone to give the excited oxygen atom O(¹D). In the upper atmosphere a particularly important source of radicals is the photodissociation of normally unreactive chlorofluorocarbons by solar ultraviolet radiation or by reactions with other stratospheric constituents. These free radicals then react with ozone in a catalytic chain reaction which destroys the ozone, but regenerates the free radical, allowing it to participate in additional reactions. Such reactions are believed to be the primary cause of depletion of the ozone layer and this is why the use of chlorofluorocarbons as refrigerants has been restricted.

Free radicals in biology

Free radicals play an important role in a number of biological processes, some of which are necessary for life, such as the intracellular killing of bacteria by neutrophil granulocytes. Free radicals have also been implicated in certain cell signalling processes^[5]. This is dubbed redox signaling.

The two most important oxygen-centered free radicals are superoxide and hydroxyl radical. They are derived from molecular oxygen under reducing conditions. However, because of their reactivity, these same free radicals can participate in unwanted side reactions resulting in cell damage. Many forms of cancer are thought to be the result of reactions between free radicals and DNA, resulting in mutations that can adversely affect the cell cycle and potentially lead to malignancy. Some of the symptoms of aging such as atherosclerosis are also attributed to free-radical induced oxidation of many of the chemicals making up the body. In addition free radicals contribute to alcohol-induced liver damage, perhaps more than alcohol itself. Radicals in cigarette smoke have been implicated in inactivation of alpha 1-antitrypsin in the lung. This process promotes the development of emphysema.

Free radicals may also be involved in Parkinson's disease, senile and drug-induced deafness, schizophrenia, and Alzheimer's. The classic free-radical syndrome, the iron-storage disease hemochromatosis, is typically associated with a constellation of free-radical-related symptoms including movement disorder, psychosis, skin pigmentary melanin abnormalities, deafness, arthritis, and diabetes mellitus. The free radical theory of aging proposes that free radicals underlie the aging process itself, whereas the process of mitohormesis suggests that repeated exposure to free radicals may extend life span.

Because free radicals are necessary for life, the body has a number of mechanisms to minimize free radical induced damage and to repair damage which does occur, such as the enzymes superoxide dismutase, catalase, glutathione peroxidase and glutathione reductase. In addition, antioxidants play a key role in these defense mechanisms. These are often the three vitamins, vitamin A, vitamin C and vitamin E and polyphenol antioxidants. Further, there is good evidence bilirubin and uric acid can act as antioxidants to help neutralize certain free radicals. Bilirubin comes from the breakdown of red blood cells' contents, while uric acid is a breakdown product of purines. Too much bilirubin, though, can lead to jaundice, which could

eventually damage the central nervous system, while too much uric acid causes gout ^[6].

Reactive oxygen species

Reactive oxygen species or ROS are species such as superoxide, hydrogen peroxide, and hydroxyl radical and are associated with cell damage. ROSs form as a natural byproduct of the normal metabolism of oxygen and have important roles in cell signaling.

Loose definition of radicals

In most fields of chemistry, the historical definition of radicals contends that the molecules have nonzero spin. However in fields including spectroscopy, chemical reaction, and astrochemistry, the definition is slightly different. Gerhard Herzberg, who won the Nobel prize for his research of electronic structure and geometry of radicals, suggested a looser definition of free radicals: "any transient (chemically unstable) species (atom, molecule, or ion)"^[7]. The main point of his suggestion is that there are many chemically unstable molecules which have zero spin, such as C₂, C₃, CH₂ and so on. This definition is more convenient for discussions of transient chemical processes and astrochemistry; therefore researchers in these fields prefer to use this loose definition.^[8]

Diagnostics

Free Radical diagnostic techniques include:

- Electron Spin Resonance

A widely-used technique for studying free radicals, and other paramagnetic species, is electron spin resonance spectroscopy (ESR). This is alternately referred to as "electron paramagnetic resonance" (EPR) spectroscopy. It is conceptually related to nuclear magnetic resonance, though electrons resonate with higher-frequency fields at a given fixed magnetic field than do most nuclei.

- Nuclear magnetic resonance using a phenomenon called CIDNP
- Chemical Labelling

Chemical labelling by quenching with free radicals, e.g. with nitric oxide (NO) or DPPH (2,2-diphenyl-1-picrylhydrazyl), followed by spectroscopic methods like X-ray photoelectron spectroscopy (XPS) or absorption spectroscopy, respectively.

- Use of free radical markers

Stable, specific or non-specific derivatives of physiological substances can be measured e.g. lipid peroxidation products (isoprostanes, TBARS), amino acid oxidation products (meta-tyrosine, ortho-tyrosine, hydroxy-Leu, dityrosine etc.), peptide oxidation products (oxidized glutathione - GSSG)

- Indirect method

Measurement of the decrease in the amount of antioxidants (e.g. TAS, reduced glutathione - GSH)

- Trapping agents

Using a chemical species that reacts with free radicals to form a stable product that can then be readily measured (Hydroxyl radical and salicylic acid)

See also

- Free-radical theory
- yl
- Reactive oxygen species
- Oxidative stress
- Mitohormesis
- Electron pair
- Unpaired electron

External links

- Free Radicals and Human Disease (<http://www.drproctor.com/crcpap2.htm>)
- Electron-transfer Factors in Psychosis and Dyskinesia--early review article (<http://www.nitrone.com/72rev.htm>)
- Ozone exposure generates free radicals in the blood samples in vitro. (http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&list_uids=9790514&dopt=Abstract)
- Oxygen Radical Absorbance Capacity (ORAC) Values of Common Foods (<http://oracvalues.com>)
- Use of Radical Emission for Determination of Ignition Delay Times (http://mark.jelezniak.de/chemical_reactions/ignition_delay_times.htm)

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- ↑ 28th International Symposium on Free Radicals[1] (<http://www.free-radicals-symposium-05.ch/index2.html>)

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Categories: Chemical bonding | Environmental chemistry | Biomolecules | Biological processes | Free radicals

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EXHIBIT B

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Formation and stabilization of persistent free radicals

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Abstract

We demonstrate that stable and relatively unreactive "environmentally persistent free radicals (PFRs)" can be readily formed in the post-flame and cool-zone regions of combustion systems and other thermal processes. These resonance-stabilized radicals, including semiquinones, phenoxy, and cyclopentadienyls, can be formed by the thermal decomposition of molecular precursors including catechols, hydroquinones and phenols. Association with the surfaces of fine particles imparts additional stabilization to these radicals such that they can persist almost indefinitely in the environment. A mechanism of chemisorption and electron transfer from the molecular adsorbate to a redox-active transition metal or other receptor is shown through experiment, and supported by molecular orbital calculations, to result in PFR formation. Both oxygen-centered and carbon-centered PFRs are possible that can

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significantly affect their environmental and biological reactivity.

Keywords: Semiquinone radical; Phenoxy radical; Cyclopentadienyl radical; Particulate matter

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Article Outline

1. Introduction
2. Experimental description
3. Results and discussion
 - 3.1. Matrix isolation studies of free radicals
 - 3.2. Calculation of PFR stabilities and reactivities
 - 3.3. Surface-induced formation and stabilization of PFRs

Further Reading

References



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EXHIBIT C

Well logging

From Wikipedia, the free encyclopedia

Well logging, also known as **borehole logging** is the practice of making a detailed record (a *well log*) of the geologic formations penetrated by a borehole. The log may be based either on visual inspection of samples brought to the surface (*geological* logs) or on physical measurements made by instruments lowered into the hole (*geophysical* logs). Well logging is done when drilling boreholes for oil and gas, groundwater, minerals, and for environmental and geotechnical studies.

Well logging

Gamma ray logging
Spontaneous potential logging
Resistivity logging
Density logging
Sonic logging
Caliper logging
Mud logging
LWD/MWD

Contents

- 1 Electric or geophysical well logs
- 2 Wireline tool types
 - 2.1 Types of electric logs
 - 2.2 History
 - 2.3 Logging While Drilling
 - 2.4 Logging measurement types
- 3 Geological logs
- 4 Wireline log
- 5 Information use
- 6 Well logging images
- 7 References
- 8 See also
- 9 External links
 - 9.1 Commercial links

Electric or geophysical well logs

The oil and gas industry records rock and fluid properties to find hydrocarbon zones in the geological formations intersected by a borehole. The logging procedure consists of lowering a 'logging tool' on the end of a wireline into an oil well (or hole) to measure the rock and fluid properties of the formation. An interpretation of these measurements is then made to locate and quantify potential depth zones containing oil and gas (hydrocarbons). Logging tools developed over the years measure the electrical, acoustic, radioactive, electromagnetic, and other properties of the rocks and their contained fluids. Logging is usually performed as the logging tools are pulled out of the hole. This data is recorded to a printed record called a "well log" and is normally transmitted digitally to office locations. Well logging is performed at various intervals during the drilling of the well and when the total depth is drilled, which could range in depths from 300 m to 8000 m (1000 ft to 25,000 ft) or more.

Electric line is the common term for the armored, insulated cable used to conduct current to downhole tools used for well logging. Electric line can be subdivided into open hole operations and cased hole operations.

Open hole operations, or reservoir evaluation, involves the deployment of tools into a freshly drilled well. As the toolstring traverses the wellbore, the individual tools gather information about the surrounding formations. A typical open hole log will have information about the density, porosity, permeability, lithology, presence of hydrocarbons, and oil and water saturation.

Cased hole operations, or production optimization, focuses on the optimization of the completed oil well through mechanical services and logging technologies. At this point in the well's life, the well is encased in steel pipe, cemented into the well bore and may or may not be producing. A typical cased hole log may show cement quality, production information, formation data. Mechanical services use jet perforating guns, setting tools, and dump bailers to optimize the flow of hydrocarbons.

Wireline tool types

Typically the wireline tools are cylindrical in shape, usually from 1.5 to 5 inches in diameter. There are three types of wireline tools:

1. With sensors without excitation

There are units to measure spontaneous potential (SP), which is a voltage difference between a surface electrode and another electrode located in the downhole instrument, other instruments that measure the natural radiation from natural isotopes of potassium, thorium, etc., to measure pressure and temperature, etc.

2. With sources of excitation and sensors

There are sensor systems consistent of a source of excitation and a sensor. In this type we find acoustic (also called sonic), electric, inductive, magnetic resonance, sensing systems, just to name a few.

3. Instruments that produce some mechanical work, or retrieve a sample of fluid or rock to the surface.

Devices to collect samples of rock, samples of fluid extracted from the rock, and some other mechanical devices.

Types of electric logs

There are many types of electric logs, and they can be categorized either by their function or by the technology that they use. "Open hole logs" are run before the oil or gas well is lined with pipe or cased. "Cased hole logs" are run after the well is lined with casing or production pipe ^[1].

Electric logs can also be divided into two general types based on what physical properties they measure. Resistivity logs measure some aspect of the specific resistance of the geologic formation. There are about 17 types of resistivity logs, but they all have the same purpose which is to measure the electric conductivity fluid in the rock.

Porosity logs measure the fraction or percentage of pore volume in a volume of rock. Most porosity logs use either acoustic or nuclear technology. Acoustic logs measure characteristics of sound waves propagated through the well-bore environment. Nuclear logs utilize nuclear reactions that take place in the downhole logging instrument or in the formation. Nuclear logs include density logs and neutron logs, as well as gamma ray logs which are used for correlation. [2].

History

Conrad and Marcel Schlumberger are considered the inventors of electric well logging. Conrad developed the Schlumberger array which was a technique for prospecting for metal ore deposits, and the brothers adopted that surface technique to subsurface applications. On September 5, 1927, a crew working for the Schlumberger brothers, lowered an electric sonde or tool down a well in Pechelbronn, Alsace France creating the first well log. In modern terms, the first log was a resistivity log that could be described as 3.5 meter upside-down lateral log [3].

In 1931, Henri G. Doll and G. Dechatre, working for Schlumberger, discovered that the galvanometer wiggled even when no current was being passed through the logging cables down in the well. This led to the discovery of the spontaneous potential (SP) which was as important as the ability to measure resistivity. The SP effect was produced naturally by the borehole mud at the boundaries of permeable beds. By simultaneously recording SP and resistivity, loggers could distinguish between permeable oil-bearing beds and impermeable nonproducing beds [4].

In 1940, Schlumberger invented the spontaneous potential dipmeter, this instrument allowed the calculation of the dip and direction of the dip of a layer. The basic dipmeter was later enhanced by the resistivity dipmeter (1947) and the continuous resistivity dipmeter (1952).

Oil-based mud (OBM) was first used in Rangely Field, Colorado in 1948. Normal electric logs require a conductive or water-based mud, but OBMs are nonconductive. The solution to this problem was the induction log, developed in the late 1940s.

The introduction of the transistor and integrated circuits in the 1960s made electric logs vastly more reliable. Computerization allowed much faster log processing, and dramatically expanded log data-gathering capacity. The 1970s brought more logs and computers. These included combo type logs where resistivity logs and porosity logs were recorded in one pass in the borehole.

The two types of porosity logs (acoustic logs and nuclear logs) date originally from the 1940s. Sonic logs grew out of technology developed during World War II. Nuclear logging has supplemented acoustic logging, but acoustic or sonic logs are still run on some combination logging tools.

Nuclear logging was initially developed to measure the natural gamma radiation emitted by underground formations. However, the industry quickly moved to logs that actively bombard rocks with nuclear particles. The gamma ray log, measuring the natural radioactivity, was introduced by Well Surveys Inc. in 1939, and the WSI neutron log came in 1941. These logs were important because they can be used in cased wells (wells with production casing). WSI quickly became part of Lane-Wells. During World War II, the US Government gave a near wartime monopoly on open-hole logging to Schlumberger, and a monopoly on cased-hole logging to Lane-Wells[5]. Nuclear logs continued to evolve after the war.

The nuclear magnetic resonance log was developed in 1958 by Borg Warner. Initially the NMR log was a

scientific success but an engineering failure. However, the development of a continuous NMR logging tool by Numar (now a subsidiary of Halliburton) is a promising new technology.

Many modern oil and gas wells are drilled directionally. At first, loggers had to run their tools somehow attached to the drill pipe if the well was not vertical. Modern techniques now permit continuous information at the surface. This is known as logging while drilling (LWD) or measurement-while-drilling (MWD). MWD logs use mud pulse technology to transmit data from the tools on the bottom of the drillstring to the processors at the surface.

Logging While Drilling

In the 1980s, a new technique, logging while drilling (LWD), was introduced which provided similar information about the well. Instead of sensors being lowered into the well at the end of wireline cable, the sensors are integrated into the drill string and the measurements are made while the well is being drilled. While wireline well logging occurs after the drill string is removed from the well, LWD measures geological parameters while the well is being drilled. However, because there are no wires to the surface, data are recorded downhole and retrieved when the drill string is removed from the hole. A small subset of the measured data can also be transmitted to the surface in real time via pressure pulses in the well's mud fluid column. This mud telemetry method provides a bandwidth of much less than 100 bits per second, although, as drilling through rock is a fairly slow process, data compression techniques mean that this is an ample bandwidth for real-time delivery of information.

Logging measurement types

Logging measurements are quite sophisticated. The prime target is the measurement of various geophysical properties of the subsurface rock formations. Of particular interest are porosity, permeability, and fluid content. Porosity is the proportion of fluid-filled space found within the rock. It is this space that contains the oil and gas. Permeability is the ability of fluids to flow through the rock. The higher the porosity, the higher the possible oil and gas content of a rock reservoir. The higher the permeability, the easier for the oil and gas to flow toward the wellbore. Logging tools provide measurements that allow for the mathematical interpretation of these quantities.

Beyond just the porosity and permeability, various logging measurements allow the interpretation of what kinds of fluids are in the pores — oil, gas, brine. In addition, the logging measurements are used to determine mechanical properties of the formations. These mechanical properties determine what kind of enhanced recovery methods may be used (tertiary recovery) and what damage to the formation (such as erosion) is to be expected during oil and gas production.

The types of instruments used in well logging are quite broad. The first logging measurements consisted of basic electrical logs (resistivity) and spontaneous potential (SP) logs, introduced by the Schlumberger brothers in the 1920s. Tools later became available to estimate porosity via sonic velocity and nuclear measurements. Tools are now more specialized and better able to resolve fine details in the formation. Radiofrequency transmission and coupling techniques are used to determine fluid conductivity (brine is more conductive than oil or gas). Sonic transmission characteristics (pressure waves) determine mechanical integrity. Nuclear magnetic resonance (NMR) can determine the properties of the hydrogen atoms in the pores (surface tension, etc.). Nuclear scattering (radiation scattering), spectrometry and absorption measurements can determine density and elemental analysis or composition. High resolution electrical or acoustical imaging logs are used to visualize the formation, compute formation dip, and analyze thinly-

bedded and fractured reservoirs.

In addition to sensor-based measurements above, robotic equipment can sample formation fluids which may then be brought to the surface for laboratory examination. Also, controlled flow measurements can be used to determine in situ viscosity, water and gas cut (percentage), and other fluid and production parameters.

Geological logs

Geological logs, use data collected at the surface, rather than by downhole instruments. The geological logs include *drilling time logs*, *core logs*, *sample logs*, and *mud logs*. Mud logs have become the oil industry standard.

Drilling time logs record the time required to drill a given thickness of rock formation. A change in the drilling rate or penetration rate usually means a change in the type of rock penetrated by the bit. The drilling time is expressed as minutes per foot, while the rate of penetration is usually expressed as feet per hour. Therefore, drilling time is the inverse of penetration rate.

Sample logs are made by examining cuttings, which are bits of rock circulated to the surface by the drilling mud in rotary drilling. The cuttings have traveled up the wellbore suspended in the drilling fluid or mud which was pumped into the wellbore via the drill string/pipe and they return to the surface via the annulus, then to the shale shakers via the flow line. Cuttings are then separated from the drilling fluid as they move across the shale shakers and are sampled at regular depth intervals. These rock samples are analyzed and described by the wellsite geologist or mudlogger.

Mud logs are prepared by a mud logging company contracted by the operating company. One parameter a typical mud log displays is the formation gas (gas units or ppm). "The gas recorder usually is scaled in terms of arbitrary gas units, which are defined differently by the various gas-detector manufactures. In practice, significance is placed only on relative changes in the gas concentrations detected^[6]." The current industry standard mud log normally includes real-time drilling parameters such as rate of penetration (ROP), lithology, gas hydrocarbons, flow line temperature (temperature of the drilling fluid) and chlorides but may also include mud weight, estimated pore pressure and corrected d-exponent (corrected drilling exponent) for a pressure pack log. Other information that is normally notated on a mud log include lithology descriptions, directional data (deviation surveys), weight on bit, rotary speed, pump pressure, pump rate, viscosity, drill bit info, casing shoe depths, formation tops, mud pump info, to name just a few.

Wireline log

A continuous measurement of formation properties with electrically powered instruments to infer properties and make decisions about drilling and production operations. The record of the measurements, typically a long strip of paper, is also called a log. Measurements include electrical properties (resistivity and conductivity at various frequencies), sonic properties, active and passive nuclear measurements, dimensional measurements of the wellbore, formation fluid sampling, formation pressure measurement, wireline-conveyed sidewall coring tools, and others. In wireline measurements, the logging tool (or probe) is lowered into the open wellbore on a multiple conductor, contra-helically armored wireline. Once lowered to the bottom of the interval of interest, the measurements are taken on the way out of the wellbore. This is done in an attempt to maintain tension on the cable (which stretches) as constant as possible for depth

correlation purposes. (The exception to this practice is in certain hostile environments in which the tool electronics might not survive the temperatures on bottom for the amount of time it takes to lower the tool and then record measurements while pulling the tool up the hole. In this case, "down log" measurements might actually be conducted on the way into the well, and repeated on the way out if possible.) Most wireline measurements are recorded continuously even though the probe is moving. Certain fluid sampling and pressure-measuring tools require that the probe be stopped, increasing the chance that the probe or the cable might become stuck. LWD tools take measurements in much the same way as wireline-logging tools, except that the measurements are taken by a self-contained tool near the bottom of the bottomhole assembly and are recorded downward (as the well is deepened) rather than upward from the bottom of the hole (as wireline logs are recorded).

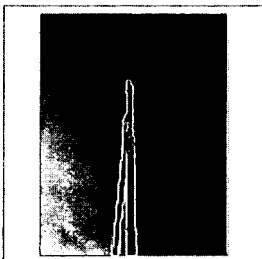
Information use

In the oil industry, the well and mud logs are usually transferred in 'real time' to the operating company, which uses these logs to make operational decisions about the well, to correlate formation depths with surrounding wells, and to make interpretations about the quantity and quality of hydrocarbons present. Specialists involved in well log interpretation are called log analysts.

Well logging images



Wireline attached to top of Christmas Tree



Oil Well Top of Wireline



Wireline Truck with drum (inside)



Wax being removed off a wireline wax knife



BO shifting tool

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See also

- Drilling mud
- Drilling rig
- Formation evaluation
- Geosteering
- List of oilfield service companies
- Log ASCII Standard
- Wireline

External links

- Society of Petrophysicists & Well Log Analysts (<http://www.spwla.org>)

Commercial links

- TecWel (<http://www.tecwel.com>)
- Petris Recall (http://www.petris.com/Products_&_Services/Data_Management/petrisewindsrecall.asp)
- Geoservices (<http://www.geoservices.com>)
- GeoloG (<http://www.geolog.it>)

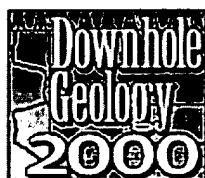
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EXHIBIT D

Quality Data, Quickly

By KATHY SHIRLEY
EXPLORER
Correspondent

Two NMR Tools Available

Today there are two NMR tool designs commercially available. While the tools are fundamentally different, both can handle most formation evaluation problems, although they may require different interpretation techniques, or in some cases need to be complemented with conventional logs.

The magnetic resonance imaging log, or MRIL, is a mandrel-type tool and was developed by NUMAR, becoming commercially available in 1991.

The petroleum industry is a business built on pushing the technological envelope, and today one of the cutting edge technologies that is changing the face of well logging is NMR, or nuclear magnetic resonance.

A lot of people might know that is happening, but not many know exactly how - or why. In fact, the very words "nuclear magnetic resonance" can humble oil company personnel with anything less than a Ph.D. in physics.

But that might be changing.

NMR experts are getting better in pointing out how the enormous benefits this technology brings to the table make the time and effort to understand and apply NMR worth the effort. Not surprisingly, NMR is beginning to hit its stride in the industry as more and more companies recognize the information this tool provides that cannot be acquired with any other technique.

"Our colleagues in the industry are basically looking to answer four questions in a reservoir," said Dave Marshall, manager of reservoir description for NUMAR, a product service line within Halliburton Energy Services.

Those questions are:

- What's the storage capacity or porosity?
- Is there a method by which those fluids can be delivered? In other words, is there permeability?
- What kind of fluids are going to be delivered?
- If hydrocarbons are delivered, will there be any water delivered as well?

"The NMR tool has the ability to answer all four questions," Marshall said. "Many people see the technology as extremely complex, but in reality it can answer all the questions that for years it has taken a whole array of tools to answer."

As Greg Gubelin, NMR products manager with Schlumberger, said, "Answers from NMR are used by the petrophysicist, geologist and



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The C series in 1994, the C-TP series in 1996 and the MRIL-Prime™ tool in 1999 followed the original NUMAR B series.

Each design provided major improvements in logging speed and acquisition capabilities. The Prime tool's logging speed is about 10-times faster than the original B series tool, and it simultaneously gathers several data sets with better repeatability.

The combinable magnetic resonance tool, or CMR, is a pad mounted tool designed by Schlumberger that was offered commercially in 1992. In 1996 the tool was upgraded to the CMR-200, a total porosity version with improved signal to noise characteristics.

Currently Schlumberger is introducing its CMR Plus tool, a major design modification that reportedly offers faster logging speeds compared to the standard CMR.

completion and reservoir engineer as an innovative way to cut coring and testing costs and to optimize completion strategies and reservoir production."

A Successful Decade

NMR techniques were first studied as early as the 1950s with the first attempt at commercial use in 1961 - but those early attempts used the earth's magnetic field, which is rather weak, so they were not wildly successful, said Brian Stambaugh, president of Houston-based NMR Petrophysics Inc.

Stambaugh authored a paper last spring for the Oil and Gas Journal on the potential benefits of NMR tools.

Schlumberger first became involved with NMR measurements in the 1960s when the company licensed a tool that was developed by Chevron.

"We designed a next generation tool that was used in the 1970s and 1980s," Gubelin said, "but it was with the advent of pulsed acquisition NMR in the early 1990s that the industry was able to take that quantum step with the technology."

The 1990s marked NMR's rebirth.

"Initially the technology was very slow, which was a drawback," Stambaugh said. "But in the early 1990s there were some successes using NMR tools in East Texas and on the Gulf Coast where conventional formation evaluation was difficult."

Those successes opened the development door.

"Industry began to see that NMR provided textural information on the rock," Stambaugh said, "much like medical MRIs provide textural information of human tissue."

NUMAR developed a mandrill type tool in the early 1990s that employed a permanent magnet and a single radio frequency, which provided effective porosity measurements that were lithology independent as well as a bulk volume irreducible component of porosity, according to Charley Siess, MRIL product manager with NUMAR.

"That's about all the tool provided in the early 1990s," Siess said, "and it was exceedingly slow, with operating speeds of about one foot per minute."

About that same time Schlumberger designed its new tool that allowed the firm to increase the logging speed and get a more accurate measurement of complete formation porosity, Gubelin said.

By 1995 the next generation of NMR tools were developed, employing multiple frequencies. These tools achieved operating speeds of up to five feet per minute and allowed for clay porosity in the measurements, which meant total porosity measurements, not just effective porosity, were possible.

"Also, with the new tools we were able to start recording multiple wait time measurements and multiple echo spacing measurements," Siess said. "These new measurements allowed NMR to move into new and different applications."

By 1997-98 NMR was becoming a primary formation evaluation instrument and consisted of nine operating frequencies with increased operation speeds.

"With these new developments we could now in a single pass do dual wait times and echo spacing measurements for direct hydrocarbon typing, as well as obtain all the fundamental reservoir properties achieved with earlier versions of the technique," Marshall said.

"We have finally reached the point where we can run NMR tools at as high a logging speed as possible while keeping the quality of the data as high as it can be."

Step-by-Step

Basically, NMR logging involves three steps, Stambaugh said.

- First, a permanent magnet aligns or polarizes hydrogen nuclei and this polarization involves an exponential buildup.
- Second, a transmitted radio frequency field manipulates the nuclei. Each radio frequency pulse "flips" the nuclei and after each flip, energy returns to the antenna or receiver coil as spin echoes.
- Finally, after the radio frequency pulsing terminates, the nuclei realign with the permanent field during the wait time.

Gubelin spoke of NMR's two key functions:

"We actually measure the response from the fluids in the pore space of the rock, so we get what's known as a mineralogy independent porosity," he said. "Also, NMR measurements give operators a producibility answer in which the porosity is broken down into its constituent parts - bound and free fluids - to get a measurement of how the formation will produce."

The two key applications for NMR logging technology are:

- Reservoir characterization, including total and effective porosity, bound and free fluid volumes, permeability, pore size distribution and clay characterization.
- Fluid characterization, which encompasses direct hydrocarbon typing or detection.

Stambaugh said log results are presented as NMR field log, integrated saturation analysis products and fluid identification from NMR.

The NMR field log generally includes NMR total and effective porosity, bound fluid or free-fluid volumes and permeability. It may also include quality control curves. The integrated saturation analysis logs uses resistivity analysis to determine whether the free-fluid volume contains hydrocarbons or water.

Marshall said the technology's most important advancements have been in the areas of improved permeability derived measurements as well as direct hydrocarbon typing.

"NMR is the first tool that allows us to directly measure permeability," he said. "Prior to the advancement of this technology whole core was the only means to get permeability information."

"Today we can directly correlate NMR downhole measurements with core laboratory measurements," he continued. "The significance of this correlation is we can make any petrophysical measurement we want in the laboratory and then take those measurements to gather the same type of information with the downhole tool, thereby building a model to use directly for the downhole tool to measure permeability."

"Prior to NMR technology there was never a reliable way to directly tie core laboratory permeability measurements with measurements from the logging tool."

Ron Bonnie, NUMAR Team One senior NMR research and applications scientist, said NMR is the only technology currently available that measures the pore size distribution of a sample and pore size distribution is what determines permeability.

NMR technology provides four direct hydrocarbon identification and saturation techniques, according to Stambaugh. The technique used depends on the tool, the formation evaluation problem and the amount of time available for logging, as well as other factors.

The four techniques provided are:

- Time domain analysis uses data recorded at two different polarization times for light hydrocarbon typing and saturation.
- Density magnetic resonance compares NMR porosity to density porosity for gas identification.
- The shifted spectrum technique uses multi-echo spacing data and is applicable in certain light-oil viscosities.
- The enhanced diffusion method uses a dual wait time with longer inter-echo spacing to enhance the oil signal's visibility and is used in direct fluid identification of light oils.

"For these methods to work properly there must be some amount of residual hydrocarbon available for measurement in the sensed volume of the NMR device," Stambaugh said. "This eliminates formations with low gas pressure, low porosity or complete flushing."

Plenty of Work Waiting

While NMR technology is beginning to catch on throughout the industry, developers are not resting on their laurels.

"Our NMR program is guided by our customer feedback," Gubelin said, adding that Schlumberger meets "regularly with NMR experts in our customers' organization's" to identify problems and needs.

Schlumberger is currently introducing its CMR Plus tool that, while maintaining the features of the CMR tool, has improved on three key features: three to five times faster logging speed, better data precision through improvements in tool hardware (the magnet, the electronics and acquisition), and the capability of logging in slimholes as small as 5 7/8 inches.

"In a recent well in the North Sea where the logging interval was about 1,000 feet, we completed the logging process in a little less than an hour," Gubelin said - a saving of about four hours.

"The savings in rig time alone was more than \$30,000," he added.

"Also, we are currently investigating deeper depth of investigation measurements, and it's our philosophy to transport all wireline measurements onto the drill pipe, so we are working on an NMR while drilling tool."

NUMAR's Siess said that "next year NMR-WD (while drilling) will be available to oil companies ... (which) will provide all the traditional NMR applications and information - but it will provide that information while drilling the borehole as well as supplemental measurements in the sliding mode, or measurement after drilling mode."

This new technique will not only provide the standard T2 measurement - the amount of time it takes for the magnetization component to deteriorate and which always has been available with NMR - but also a T1 measurement, which is the amount of time it takes for the magnetization component to occur.

"Also, NMR while drilling allows us to take NMR measurements early in the process, before the affects of invasion," he said. "Plus, NMR-WD, like any measurement while drilling technique, provides time and cost savings to a project."

Another technological advancement scheduled for commercial use in 2001 is a magnetic resonance fluids analyzer. This instrument will be part of a new reservoir description tool and will essentially make laboratory quality T1 type measurements in reservoir conditions.

For example, he said, an institute in France that monitors the quality of wines made all over the country has acquired a few NMR spectrometers. They run the wines through the spectrometer and can not only tell which winery the wine is from but whether the grapes were grown on the north flank of a mountain or the south flank.

"This technology is that much more discriminating than optical analyzers," he said.

Marshall said NUMAR has been preparing a catalog of mud filtrates to use for comparative purposes in conjunction with the new magnetic resonance fluids analyzer.

The intent is to take measurements on fluids as they come into the formation test tool, monitoring the change and very clearly determine when we are at optimum clear sample.

"Ultimately this should lead to directly providing measurements of viscosity and gas-oil ratio," Marshall said, "which in turn can be incorporated into a company's producibility and rates predictions, how they set facilities and what type of facilities they set."

Looking Ahead

Continuing technological advancements and education make the future for NMR tools very bright.

"We continually work with clients to show what NMR can do," Siess said. "Typically, after they see the benefits for themselves they are sold. But, honestly, it has taken more time than any of us anticipated to educate the industry on the advantages."

NUMAR recently established a team approach, providing a group of experts to help clients determine objectives and define how NMR can help.

Gubelin said Schlumberger did the same.

"We have a network of experts," he said. "This group's chief responsibilities are making sure every job is properly pre-planned, acquisition and interpretation is handled correctly, and to follow-up with customers."

The company has done about 4,000 NMR logging jobs in the last four years, from China to the North Sea to Venezuela, Gubelin said.

"The service companies are unwavering in their belief of the power of this tool," Siess added. "Halliburton (is) aware that it will take time to establish the fundamental change in thinking that will lead to common use of NMR tools, and every day we work on new ways to cross the chasm with this new technology."

Stambaugh said all the major service companies have large staffs focused on NMR, so this technology should evolve quickly.

"NMR is by no means fully developed," he said, adding that there will be "major improvements" in areas such as better bed resolution and advances in fluid identification.

"We must continue to advance the technology, prove the value of the measurement and deliver complete service," Gubelin said, "and NMR will reach its full potential."